

PATENT SPECIFICATION

(11) 1322724

1322724

NO DRAWINGS

- (21) Application No. 1737/73 (22) Filed 12 June 1969
 (62) Divided out of No. 1322722
 (23) Complete Specification filed 29 May 1970
 (44) Complete Specification published 11 July 1973
 (51) International Classification C01F 7/00 C01B 25/36
 (52) Index at acceptance
 C1A D10 D37 G4 G4D10 G4D37
 (72) Inventors JAMES DEREK BIRCHALL and
 JOHN EDWARD CASSIDY



(54) COMPLEX ALUMINIUM PHOSPHATES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel phosphates and to their preparation, and in particular to complex phosphates of aluminium. We have found that certain complex phosphates of aluminium are especially useful for preparing fibres, coatings, binders and fine particles of aluminium phosphate.

According to the present invention there is provided a solid water-soluble halogen-containing complex phosphate of aluminium wherein the ratio of the number of gram atoms of aluminium to the number of gram atoms of phosphorus is substantially 1:1 and which contains at least one chemically-bound molecule of water.

The halogen in the halogen-containing complex phosphate of aluminium is preferably chlorine, but the compounds may contain other halogens, for example bromine or iodine.

The ratio of the number of gram atoms of aluminium to the number of gram atoms of phosphorus in the complex phosphates of aluminium is substantially 1:1. The complex phosphates of the invention decompose at low temperatures and, because they have this ratio, directly form normal aluminium orthophosphate which has good chemical stability and refractoriness. The ratio of the number of gram atoms of aluminium to the number of gram atoms of halogen in the complex phosphates is preferably substantially 1:1.

The complex phosphates of the invention may be monomeric or polymeric.

The monomeric forms, or the repeating units of the polymeric forms of the complex phosphates, may contain, for example, from one to five molecules of water. Most frequently the number of molecules of water is 4.

quently the number of molecules of water is 4.

An example of a complex phosphate containing chemically-bound water is the complex phosphate containing chemically-bound water having the empirical formula $Al_2PCl_2H_4O_8$. The infra-red and X-ray characteristics of the compound are as hereinafter described. This compound is designated aluminium chlorophosphate hydrate, for convenience referred to as ACPH, but it is to be understood that this designation in no way implies any particular molecular structure for the compound.

The complex phosphates of the invention are soluble in water. Solvents comprising water and a water-miscible organic solvent are especially convenient for dissolving the complex phosphates. Solubility generally increases as the pH of the solution is decreased, and it is preferable to establish a pH of less than 2.5 in water solutions to maintain maximum solubility. The compounds of the invention generally give viscous solutions in water.

The complex phosphates of the invention may be prepared, for example, by reacting an aluminium compound, preferably a halide, with water and phosphoric acid or a compound capable of forming phosphoric acid under the reaction conditions, and, when an aluminium compound other than a halide is used, a halogen acid, and separating the complex phosphate as a solid product.

The aluminium halide may be a simple halide or an oxyhalide or an aluminium alkoxy halide, for example aluminium ethoxy chloride. Other suitable aluminium compounds include aluminium alkoxides, for example aluminium ethoxide. When an aluminium compound other than a halide is used, the presence of a halogen acid is necessary. Aluminium and a halogen acid may be used to form an aluminium halide in situ.

Compounds capable of forming phosphoric acid include phosphorus pentoxide, phosphorus oxyhalides and phosphorus halides.

An aqueous solution of phosphoric acid may be used, conveniently an 88% solution in water.

5 The order in which the reactants are added to one another is not critical; we prefer to add the aluminium compound to the water and then to react phosphoric acid with the resultant mixture.

10 The highest yields of product are obtained when the molar ratio of aluminium to phosphorus in the reaction is substantially 1:1.

15 The reaction may be carried out over a wide range of temperature, but generally we prefer to use a temperature below 60° C and preferably from 0° C to 50° C, to obtain optimum yields.

20 Complex phosphates according to the invention containing chemically-bound water molecules or mixtures containing the said complex phosphates may also be prepared by the hydrolysis of complex halogen-containing aluminium phosphates wherein the ratio of the number of gram atoms of aluminium to the number of gram atoms of phosphorus is substantially 1:1 and which contain at least one
25 chemically-bound molecule of an organic hydroxy compound. These complex phosphates are described in our copending UK Patent Application 29862/69 (Serial No. 1322722) from which the present patent application has been divided. By hydrolysis, it is possible to replace the organic hydroxy compound with water molecules. It is especially convenient to use as starting material the
35 complex phosphate having the empirical formula $\text{Al}(\text{PClH}_2\text{C}_2\text{O})_3$. Hydrolysis may be effected by any convenient means, but for many of the starting compounds it is sufficient to add water at room temperature or to keep the compounds in contact with moist air for a sufficient time. Conveniently this is done by fluidising the compound in a stream of humidified air, preferably at a temperature below 80° C.

45 When the complex phosphate is prepared in solution, it is separated from the reaction mixture and used as such or optionally further purified before use. Separation of the product may be effected by any convenient means, for example by precipitation by cooling, evaporation of volatile constituents or addition of a further component, followed by filtration or by chromatography. The mother liquor left after separation of the product may
55 be discarded or recycled for further use, preferably after purification from unwanted side-products of the reaction.

60 The complex phosphates according to the invention decompose on heating to give aluminium phosphate in amorphous or various crystalline forms. The temperature at which aluminium phosphate forms depends upon the particular complex phosphate heated, but is normally from 80° C to 500° C, and is often below 100° C. It is convenient to heat the

complex phosphate to a temperature from 100° C to 150° C to form aluminium phosphate. Surprisingly, crystal forms of aluminium phosphate can be obtained at low temperatures which are normally obtained only
70 by heating aluminium phosphate to temperatures in excess of 800° C. The aluminium phosphate may be further heated, for example to change its crystalline form.

75 The compounds of the invention thus provided a source from which aluminium phosphate may be produced in many desirable forms at low temperatures, conveniently from solutions of the complex phosphates in water. The complex phosphates of the invention are therefore especially useful for producing, for example, formed bodies, coatings and binders comprising aluminium phosphate. The properties of aluminium phosphate are such as to confer on these materials desirable properties
85 such as strength, refractoriness or chemical inertness.

Solutions containing complex phosphates according to the invention may conveniently comprise additional components, for example materials which will aid the further processing of the solutions or desirably affect the products formed from the solutions. Thus organic materials, especially polymers, may be dissolved in the complex phosphate solution. Additional components, for example pigments, colorants or fillers, may likewise be dispersed in the solution of the complex phosphates. Aqueous solutions of complex phosphates of the invention may contain crystallisation stabilisers, for example finely divided silica or alumina, or nucleation activators or catalysts, for example dibutyl peroxide, or calcium, magnesium or sodium chloride.
105

Solutions of the complex phosphates, especially aqueous solutions, are viscous, so that fibres may be prepared from them by one of the usual fibrising processes such as drawing, blowing, extrusion through a spinneret or centrifugal spinning. The use of the solutions in the preparation of fibres is described in our copending UK Patent Application 2791/73 (Serial No. 1322725) which, like the present application, is a divisional from UK Patent Application 29862/69 (Serial No. 1322722).
110

Solutions of the complex phosphates may also be used to produce coatings of aluminium phosphate on surfaces, by removal of solvent from the solution and preferably heating of the deposited coating. The use of the solutions for coating surfaces is described in our copending UK Patent Application 3344/73 (Serial No. 1322726), also a divisional from UK Patent Application 29862/69 (Serial No. 1322722).
115

Furthermore, a solution comprising one or more of the complex phosphates may be used as an adhesive or binder for a wide variety
120 130

of materials. It is especially useful as an adhesive or binder for siliceous materials, for example sand or glass; metal especially metal powder and ceramic materials generally, for example alumina or carbon. The adhesive bond may be strengthened by heating preferably to temperatures between 200° C and 1000° C, after removal of solvent and initial curing at 100° C to 200° C of the adhesive or binder.

Strong, thermally stable and chemically inert resistant composite materials may be prepared by incorporating aligned or random fibres, for example glass fibre, carbon fibre, silicon carbide fibre or asbestos with a desired quantity of a solution of the complex phosphates, removal of the solvent, initial curing at 100° C. to 200° C and preferably further heating, for example to a temperature of from 200° C to 1000° C.

The complex phosphates may also be used to prepare fine particles of aluminium phosphate by rapid heating of the bulk material to a temperature greater than 900° C, and grinding the resultant mass. Fine particles produced in this way may advantageously be used as a reinforcing filler in polymers such as polyvinyl chloride or they may be incorporated into molten glass as a nucleating agent in the preparation of nucleated glass.

The invention is illustrated but not limited by the following Examples:—

Example 1

15.2 gram of anhydrous aluminium chloride was added slowly to 40 ml of distilled water. The resultant solution was cooled to ambient temperature and 7.4 ml of an 88% solution of orthophosphoric acid added to it with stirring. The solution was then concentrated by heating to a volume of about 20 ml. A viscous yellow-brown liquid was formed which, after several days' standing in a crystallising dish, produced a crop of crystals. The crystals were filtered off, washed with ethanol and dried in a vacuum dessicator. The chemical analysis of the crystals gave aluminium 10.6% by weight, chlorine 14.5% by weight, phosphorus 12.4% by weight, water 40.1% by weight. The analysis corresponded well with the empirical formula $\text{AlPClH}_{11}\text{O}_8$. The X-ray powder pattern was obtained for the crystals using a Philips powder camera, $\text{CuK}\alpha$ radiation and a nickel filter.

The intensities were obtained by visual observation, and the data are shown in Table I:

TABLE I

Intensity	Value
s	9.20
vw	7.31
w	6.68

vw	5.78	
vw	5.50	
vw	5.02	
w	4.55	65
w	4.24	
w	4.08	
w	3.931	
w+	3.705	
w-	3.504	70
w	3.411	
w	3.276	
w+	3.184	
w+	3.123	
m	3.030	75
m-	2.966	
w	2.886	
w	2.824	
w-	2.676	
w-	2.600	80
w+	2.427	
w	2.263	
w	2.225	
vw	2.141	
m	2.094	85
vw	2.062	
vw	2.023	
w-	1.979	
w	1.914	
vw	1.850	90
w	1.819	

s=strong; v=very; w=weak; m=medium

Example 2

A halogen-containing complex phosphate of aluminium containing chemically-bound alcohol was prepared and hydrolysed.

40 gram of anhydrous aluminium chloride was added to 300 ml of laboratory grade ethyl alcohol. The resultant solution was cooled to 0° C and 18.6 ml of 88% orthophosphoric acid was added to it in a drop-wise manner and the reaction mixture stirred. The reaction was carried out in an atmosphere of dry nitrogen. The white crystalline material formed was separated from the mixture, washed with ethanol and dried under vacuum at a temperature of 0° C. 70 gram of product was obtained, and was found, by analysis, to have the empirical formula $\text{AlPClH}_{22}\text{C}_4\text{O}_8$.

10 gram of the compound produced was placed in a tray to a depth of 1/4-inch and left for 6 days at a temperature of 20° C. and in a relative humidity of 75%.

The resultant amorphous product contained 0.1% by weight of chemically-bound ethyl alcohol and 35.1% by weight of chemically-bound water. The compound contained 11.32% by weight of aluminium, 12.70% by weight of phosphorus and 11.84% by weight of chlorine.

Example 3
300 gram of the compound



5 prepared as described in Example 2 was placed in a 4-inch diameter tube fitted with a No. G2 glass sinter near its base. Compressed air was blown through the compound at a rate of 20 litres per hour for 92 hours. A dry amorphous powder was formed containing 12.4% by weight of aluminium, 11.6% by weight of chlorine, 14.5% by weight of phosphorus and 30% by weight of chemically-bound water.

10 A differential thermal analysis of a sample was carried out. The thermogram showed two endothermic peaks at about 108° C to 160° C.

WHAT WE CLAIM IS:—

20 1. A solid water-soluble halogen-containing complex phosphate of aluminium wherein the ratio of the number of gram atoms of aluminium to the number of gram atoms of phosphorus is substantially 1:1 and which contains at least one chemically-bound molecule of water.

25 2. A complex phosphate as claimed in claim 1 wherein the halogen is chlorine.

30 3. A complex phosphate as claimed in claim 1 or claim 2 wherein the ratio of the number of gram atoms of aluminium to the number of gram atoms of halogen is substantially 1:1.

4. A complex phosphate as claimed in any one of the preceding claims which contains from 1 to 5 molecules of water.

35 5. A complex phosphate as claimed in claim 4 which contains 4 molecules of water.

6. A complex phosphate as claimed in claim 1 having the empirical formula $\text{AlPClH}_{11}\text{O}_4$.

7. A method of preparing a complex phosphate as claimed in any one of the preceding claims comprising the step of interacting an aluminium compound with water and phosphoric acid or a compound capable of forming phosphoric acid under the reaction conditions and, when an aluminium compound other than a halide is used, a halogen acid, and separating the complex phosphate as a solid product.

8. A method as claimed in claim 7 wherein the aluminium compound is aluminium chloride.

9. A method as claimed in claim 7 or claim 8 wherein the molar ratio of aluminium to phosphorus in the reaction mixture is substantially 1:1.

10. A method of preparing a complex phosphate as claimed in any one of claims 1 to 6 which comprises hydrolysing a halogen-containing complex phosphate of aluminium wherein the ratio of the number of gram atoms of aluminium to the number of gram atoms of phosphorus is substantially 1:1 and which contains at least one chemically-bound molecule of an organic hydroxy compound.

11. A method as claimed in claim 10 wherein the complex phosphate used as starting material is the complex phosphate having the empirical formula $\text{AlPClH}_{11}\text{C}_2\text{O}_4$.

12. A method of preparing a halogen-containing complex phosphate of aluminium substantially as described in any one of the Examples.

13. A complex phosphate whenever made by a method claimed in any one of claims 7 to 12.

ANTHONY C. HALLIWELL,
Agent for the Applicants.